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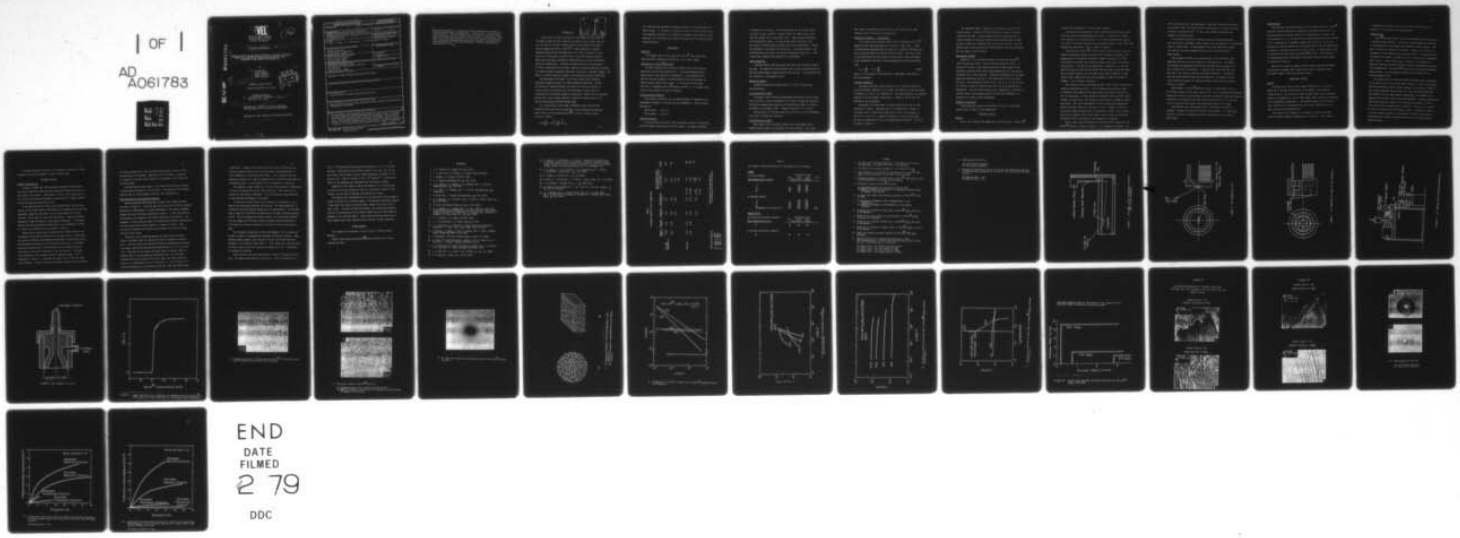

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An experimental characterization and processing study of redissolved Kevlar® and poly(p-phenylene terephthalamide)/sulfuric acid solutions is reported. Polarized light microscopy studies show the development of an anisotropic phase. When two phases coexist, negatively birefringent spherulites are observed. At higher concentrations, a single phase of coalescing spherulites is seen and following melting and subsequent cooling, nematic (threadlike)

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structures are observed. Viscosity and normal stresses were measured at various concentrations and temperatures. A yield stress is exhibited at room temperature. Both room temperature and 60 degree C viscosity versus concentration curves display maxima. The solutions in concentration ranges from 2 to 12% have been extruded as ribbons and as annular blown tubular film. Processing variables and problems are discussed. Wide angle x-ray scattering patterns of films show orientation. Tensile properties have been measured on films.

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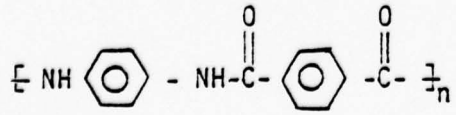
INTRODUCTION

A most striking recent technological development was the invention by Kwolek, Morgan and their coworkers at DuPont (1-7) of super high modulus and tensile strength filaments from p-linked aromatic polyamides and the commercialization of Kevlar®. These researchers indicate enhanced properties are developed due to the liquid crystalline characteristics of the polymer solutions used in the fiber formation process. These views have been confirmed by investigations in our own laboratories. (8) and by Celanese (9). Following the above efforts, the development of similar characteristics have been reported by Tennessee Eastman and DuPont for largely aromatic polyesters where melt processing is possible (10-12). Recently a critical review of polymer liquid crystals has been written (13).

The development of polymer liquid crystal based fiber formation technology suggests extension to other processing operations. Jackson and Kuhfuss of Tennessee Eastman (10) report the injection molding of liquid crystalline polyesters and the development of high levels of orientation and anisotropic mechanical properties. Miyoshi and his coworkers Unitika (Uji, Kyoto, Japan) describe a process for making tubular film from poly(p-phenylene terephthalamide).(14).

It is the purpose of this paper to present a basic study of the characterization and solution processing of poly(p-phenylene terephthalamide) (PPD-T) and redissolved Kevlar®, believed to have the same structural formula:



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Our investigations represents a progress report of a continuing study of these systems. It includes (i) structural studies of the solutions using electromagnetic radiation, (ii) rheological property investigations of the solutions (iii) and fabrication studies of sheet and film along with their characterization.

EXPERIMENTAL

Materials

The polymers used in this study were Kevlar® fiber supplied by DuPont and PPD-T supplied by Unitika Ltd. (Uji, Kyoto, Japan)

Dissolution of Kevlar® and PPD-T

The above samples were dissolved in 100% sulfuric acid using an electrically driven high speed stirrer. The mixing temperature was usually kept in the range 60 to 80 degrees C. The concentration of sulfuric acid was checked by titration before mixing and adjusted to 100% by adding fuming sulfuric acid. It is easier to form a dope with PPD-T as opposed to Kevlar® because the PPD-T is in a powder form, and also less crystalline and not oriented.

Dilute Solution Viscosity

The intrinsic viscosity, $[\eta]$, of these polymers was measured in an Ubbelohode viscometer in sulfuric acid at 30 degrees C. The $[\eta]$ values obtained are

Kevlar fiber: $[\eta] = 6.2$

PPD-T powder: $[\eta] = 4.5$

Optical Microscopy

A Leitz Ortholux polarizing light microscope was used to investigate the birefringent characteristics of the systems. The sample thickness

is controlled in two ways. For the measurement of the thicker sample solutions, Fisher Scientific Littman Slides (for fungus mounts) were used and covered with a glass cover slide. These possess depressions of thickness 600 microns. For the thinner sample solutions, cells were made by pressing samples between glass plates separated by a spacer. The thickness of the spacer was 100 microns. The sample holder of the microscope had a hot stage with accurate temperature regulation. Transmitted light intensity was measured with a photometer.

Light Scattering

A Spectra-Physics 130B helium-neon gas laser with wavelength 6328 Å was used. The sample was placed between glass slides as indicated earlier and positioned between crossed polarizer and analyzer. The scattered light was recorded on a photographic plate.

Absorption Spectra

Absorption spectra were determined with a Cary 17 double beam spectrophotometer.

X-ray Diffraction (WAXS)

Wide angle x-ray diffraction measurements were made on the solutions using a Philips X-ray diffractometer with nickel filtered CuKα radiation. The solution samples were placed in thin walled glass tubes to minimize the effect of the sample holder. Exposure times were for 2-4 hours.

WAXS patterns of films were made using a Philips x-ray diffractometer with nickel filtered CuKα radiation.

X-ray Diffraction (SAXS)

Small angle x-ray diffraction behavior was investigated using a Rigaku rotating anode X-ray generator with CuKα radiation. As in the

WAXS studies the samples were contained in thin walled glass tubes. Exposure times of 6 hours or more were used.

Rheological Property Measurements

The viscosity and principal normal stress difference of Kevlar® / H_2SO_4 solutions were determined as a function of shear rate. A model R-16 Weissenberg Rheogoniometer was used with a specially designed cone-plate system machined from type 304 stainless steel. The shear stress σ_{12} was determined from the torque T and the normal stress difference N_1 was determined from normal force measurements using the expressions (15):

$$\sigma_{12} = \frac{3T}{\pi R^3} ; \quad N_1 = \frac{2F}{\pi R^2} \qquad (1a,b)$$

where R is the radius of the cone-plate. Measurements were made at 25 and 60 degrees C.

Extrusion Apparatus

The polymer solutions were extruded to form ribbon and sheet/film from two different apparatus. One of these was identical to that developed by Hancock et al (8) in our laboratories. The second apparatus was designed especially for the present investigation. Figures 1a and 2a show the features of this equipment.

Rectangular slit dies shown in Figure 1b were mainly used for the formation of ribbons. These were used in the apparatus of Figure 1a. The aspect ratio of these dies ranges from 4 to 30. The thickness of the die slit is 0.2 mm. A specially designed die with an annular gap was used to produce wider films in the apparatus of Figure 1a. This die is shown in Figure 1c.

The apparatus shown in Figure 2a is essentially a tubular film blowing system. A tubular film die allowing for internal inflation (Figure 2b) was used. The main objective of this apparatus was to radially expand the extrudate through the dies annular gap with pressurized nitrogen gas introduced from the outlet of the die. Thus the emerging tube may be continuously drawn biaxially via radial expansion and simultaneous winding tension.

Degradation Problems

Generally it is a difficult process to dissolve the Kevlar® fibers because they are in a highly oriented crystalline state. In the case of forming a high concentration dope, rather severe mixing conditions including both a high mixing temperature and a long mixing residence time is often required. Significant degradation of the sample under such conditions can occur. The fiber originally has an $[\eta]$ of 6.2 dl/g. This decreased to values of 5.2, 4.8, 4.2, 1.4, and 0.5 dl/g. in a series of tests to determine the effect of mixing conditions on degradation. Controlling the sulfuric acid concentration rigorously to 100% and using a mixing temperature of no more than 60 degrees C is favorable for avoiding severe degradation.

Mechanical Properties

Force-elongation curves were obtained on films in a Table Model Instron Tensile Tester at room temperature.

STRUCTURAL STUDIES

Results

Let us first consider the appearance of the solutions. The Kevlar®

solutions are dark brown in color and nearly opaque.

The polarizing microscope was used to determine the conditions under which the solutions studied became anisotropic. The solutions studied were isotropic at low concentrations. In a narrow concentration range of 9 to 9.5%, a transition occurred to an anisotropic phase in which light came through the cross polars. This is shown in Figure 3.

The solutions of Kevlar® in the transition region (9~9.5%) from isotropic to anisotropic appear to exhibit small globular structures. The average size of the globular particles is about 5 microns (5×10^4 Å). The particles are spherulites showing a Maltese cross under cross polars (see Figure 4). The sign of the spherulites is negative, i.e., the tangential refractive index must be greater than the radial refractive index. The anisotropic phase of this two phase region (9~9.5 weight %) is composed of small spherulites that form aggregates of about 50 microns in diameter. This is shown in Figure 5a.

The structure of the single phase polymer liquid crystalline solutions cannot be characterized easily. This is because the anisotropic phase is affected by the shearing force applied when the sample is placed in a cell for microscopy. As the orientation relaxation time of polymer liquid crystals is quite long, a rest period of several days is needed to acheive equilibrium. The size of the domains of the as-formed room temperature wholly anisotropic phase are very small (< 10u). However, threadlike structures resembling those found in low molecular weight liquid crystals (16, 17) are observed after the as-formed liquid crystalline structures are melted at 90°C and cooled to room temperature (Figure 5b).

The H_v (laser light scattering with cross polarizer) pattern for the Kevlar® solution is shown in Figure 6. It is complex in character. As

the solution consists of the aggregates of many small sperulitic particles, the scattered light is affected by the birefringence of the other particles existing in the optical path. In this case, multiple scatterings are supposed to inevitably occur.

In anisotropic solutions, absorption spectra sometimes associated with the pitch of cholesteric liquid crystals were not observed in a wavelength range of visible light. At wavelengths of less than 4200 Å such absorption spectra could not be detected owing to the strong absorption of phenyl groups.

When polymer solutions are investigated by x-ray diffraction, much attention must be paid to the selection of the sample cell. The sample cell absorbs the scattered x-ray and also diffracts the x-ray beam by itself to exhibit an x-ray pattern. A very thin wall glass capillary cell was used in this study to minimize the effect of the cell. Diffraction from the solvent molecules must be considered too. The analysis of the x-ray diffraction patterns of lyotropic polymer liquid crystals has many difficult problems.

WAXS patterns of Kevlar® solutions exhibit a strong inner ring at 10~15 Å and a weak, diffuse outer ring at 4.6 Å. No distinguishable difference between the isotropic and anisotropic solutions was observed from those patterns. Considering the scattering from the solvent and sample cell, it is very difficult to quantitatively explain the experimental data at this stage.

SAXS patterns were also measured for all anisotropic solutions of polymers. However, no distinct diffraction was obtained. It is concluded from this fact that no repeating structural feature exists in the 60 to 300 Å range.

Interpretation

The polarized light observations of the two phase regions of Kevlar® solutions show the existence of negatively birefringent spherulites. As the polarizability along the length of the aramide chain is greater than that perpendicular to it, we may conclude these macromolecules are oriented in a circumferential or tangential manner (See Figure 7a). While polyethylene also exhibits negatively birefringent spherulites (18, 19) and this is generally considered to be due to chain folding, the SAXS patterns give no indication of chain folding for Kevlar® solutions. The orientation of the macromolecules in the nematic structure of the anisotropic phase is surmised in Figure 7b.

Many of the structural aspects of these systems have been developed in more detail elsewhere (20), where we have made a comparative study with other polymer liquid crystalline solutions.

RHEOLOGICAL STUDIES

Results

Viscosity and principal normal stress difference as a function of shear rate at various concentrations at 25 degrees C are plotted in Figures 8 and 9. The viscosity at very low shear rates is an increasing function of concentration, but at higher shear rates a maximum is exhibited at an intermediate concentration. The viscosity-shear rate function is nearly Newtonian at low concentrations, but rises indefinitely at low shear rates and high concentrations.

The viscosity at 60 degrees C is plotted as a function of shear rate for several different concentrations in Figure 10. The viscosity

is Newtonian at low shear rates in all cases, but still exhibits a maximum in its viscosity versus concentration.

Interpretation

Kevlar® solutions exhibit many of the rheological characteristics of common polymer solutions. The overall viscosity-shear rate behavior is non-Newtonian and the systems show signficant normal stresses. However, the detailed character is different. Notably, the viscosity at 25 degrees C rises indefinitely at low shear rates. To pursue the significance of this Figure 11 presents a plot of viscosity as a function of shear stress. A yield stress value is observed. Also Papkov et al (21) have noted the occurrence of yield values in concentrated solutions of p-polybenzamide. Thus Kevlar®/sulfuric acid solutions and perhaps other aramides at room temperature behave as gels rather than as ordinary polymer fluids.

The concentration at which the viscosity maximum occurs corresponds to the onset of the liquid crystal phase formation. Similar observations have been reported by Kwolek and her coworkers (1, 5, 6) for a range of para linked polyamides and by Papkov et al (21) for poly(p-benzamide). Such behavior has also been found by Hermans (22) for synthetic polypeptides which exhibit liquid crystalline character. However, quantitative conclusions about this aspect of the rheology of aramides in sulfuric acid solution must be approached with caution. Viscosity is a function of both the concentration and molecular weight. The molecular weight, via amide linkage cleavage in the presence of sulfuric acid, must unquestioningly be lowered as shown by the intrinsic viscosity results mentioned above.

A detailed comparative study of the rheological properties of these solutions with other polyamides is given elsewhere (23).

EXTRUSION STUDIES

Process Considerations

A range of ribbons and films have been extruded vertically downward into a water bath where they were coagulated through extraction of the sulfuric acid solvent. (See Figures 1 and 2). After being wound up on a roller, the samples were washed or neutralized in a weakly alkaline (pH 8-9) solution and then dried in air.

It was found during the ribbon spinning experiments that the cross section of the ribbon deforms significantly as it emerges from the die and coagulates, especially when there is an air gap between the die and the bath. With a large air gap, more than 50 mm, it seems to be almost impossible to keep the sample's cross section rectangular. In the most extreme case the end product has been found to be a completely cylindrical fiber, very different from the contour of the die.

Making the air gap as small as possible was the most effective way to prevent or minimize the distortion of the cross section. Other important factors related to this problem are presumably the extrusion rate V_o and the take-up velocity V_1 or the draw down ratio V_1/V_o. It has been found that spinning with a lower extrusion rate and larger draw down ratio tends to avoid the distortion of the cross section. The higher the concentration, the narrower the useful operating range. This is summarized in Figure 12. Increasing the aspect ratio of the slit seems to be effective. The main factors which appear related to this distortion

are large extrudate swell due to unconstrained elastic recovery and the surface tension of the dopes. Apparently the first factor is dominant as witnessed by the more serious nature of the problem in the higher concentration dopes.

A problem which arises notably in the tubular film extrusion process is associated with bubbles in the solutions. The presence of such bubbles tends to lead to 'burst through' failure of the inflating film.

Characterization of the Extrusion Products

Scanning electron photomicrographs of some of the ribbons produced are shown in Figure 13. It may be seen that one of the distinctive features observed with these photos is a great difference in the surface roughness between the lower and higher concentration samples. A scale structure can be observed on the surface of the ribbon formed from a 2% solution. This roughness or scale structure seems to be diminished at higher concentrations. The high concentration samples appear as a bundle of fibrils. Some structural differences would seem to exist between the central and edge portions of the ribbon.

Wide angle x-ray scattering patterns for some films are shown in Figure 14 and other data for ribbons and films are reported in Tables 1 and 2. They are crystalline and many of them are preferentially oriented. The primary reflections observed have Bragg spacings of 3.2 Å, 4.0 Å and 5.0 Å. According to the crystal structure models of Northolt (24) and Tadokoro (25) for poly(p-phenylene terephthalamide), the calculated strongest reflections should be the (110), (200), and (004) reflection planes of an orthorhombic unit cell (see Table 1). The 3.2 Å and 4.0 Å spacings correspond to the reflections from their (004) and (200) planes,

respectively. However, the strong reflection of the 5.0 Å spacing cannot be assigned by their crystal structure model (the Bragg spacing of (110) reflection is 4.32 Å from their model). This reflection was also observed by Hancock et al (8) who suggested that it might be associated with a polymorphic form. A not dissimilar view is expressed by Jaffe (9).

The uniaxially drawn ribbon and film show strong equatorial intensities for the 5.0 Å spacing but not the (200) reflection. The intensities increase with the extent of draw down. The 5.0 Å spacing is most sensitive to the orientation developed in the sample.

In the case of blown tubular film, preferential orientation to the machine and transverse directions was observed. The sharp equatorial reflection of the 5.0 Å spacing planes was also characteristic. On the other hand, a weak (110) reflection was detected at the Bragg reflection spacing 4.32 Å. The (110) planes also sharply locate in the transverse direction. This may suggest that the b-axis tends to become oriented perpendicular to the machine direction as observed in the melt spinning of polyolefins (26).

The influence of annealing at 400 to 500 degrees C for 10 minutes can be seen in terms of a sharpened and increased diffraction intensity. Some annealed samples showed a new diffraction ring at 7.63 Å when they were annealed in a silicone oil bath (Table 1). This reflection is not predicted by Northolt (24) but was also observed by Hancock et al (8). Orientation is increased by annealing.

Stress-strain curves were determined for ribbons in the machine direction. The samples were generally very brittle. Tensile strengths of 0.5

to 5.0 x 10^8 dynes/cm^2 were obtained and elongations of 1.5 to 14% were obtained. These samples were produced without an air gap. Dry jet wet spun fibers from the same solutions showed substantial increases in properties, e.g. a tensile strength of 240 x 10^8 dynes/cm^2. A contributing factor to the weaknesses was degradation of the molecular weight.

Annealing of the ribbon at 400 to 500 degrees C for 10 minutes was not found to have any substantial effect on the tensile strength of the ribbons, but was found to decrease the elongation to break.

The stress-strain characteristics of a dry jet blown film are shown in Figure 15, along with a non-blown sample. The improved transverse strength of the blown film clearly can be seen here, though its blow-up ratio is small (1.2X). The ratio of tensile strength in the transverse direction and also in the machine direction almost doubles when the blown sample is compared to the non-blown sample. After annealing both the blown and unblown samples show a much improved tensile strength in both directions.

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TABLE 1

D-SPACINGS (WAXS) OF PPD-T RIBBON/FILM

	Weight Percent Solution Concentration					Wet Spun Redissolved Kevlar Fiber, Hancock et al (8)	Rings
	2%	4	8	12			
Extruded Ribbon/Film	3.22Å	3.22	3.25	3.27		3.22	004
	4.00	4.00	3.96	7.95		3.97	200
			5.14	5.03		4.97	
						7.59	
Annealed	3.22	3.22	3.27	3.31	(3.31)*	3.19	004
	4.00	4.00	3.97	3.95	(4.07)*	3.98	200
						4.35	110
			5.04	5.04	(5.00)	5.08	
					(7.63)	7.63	

Annealing conditions.

2% 300°C x 10^{min}
4 500°C x 10^{min}
8 400°C x 10^{min}
12 400°C x 8^{min}

*(Parentheses indicate annealing in a silicone oil for six minutes)

TABLE 2

Half angles of WAXS diffraction arcs as measured from the equator.

RIBBON

a) As Spun Samples

Dope Concentration, (wt.%)	Diffraction Plane (110)	(200)	(004)	7.6 Å
	angles are in degrees			
2		180	180	
4	65	180	180	
8	60	180	180	
12	60	180	180	

b) Annealed Samples

2		180	180	
4	65	180	180	
8	40	180	180	
12	30	180	180	
12 (annealed in silicone oil)	30	180	180	180

TUBULAR FILMS

a) As Spun with Uniaxial Extension

Dope Concentration (wt.%)	Diffraction Plane (110)	(200)	(004)
	angles are in degrees		
11	28	180	180

b) As Spun with Biaxial Extension

12	23	37	30

FIGURES

1. (a) Small scale extrusion apparatus. (b) Ribbon slit die used in the apparatus. (c) Annular die used in the apparatus.

2. (a) Tubular film extrusion apparatus. (b) Tubular film die.

3. Light intensity as a function of concentration for Kevlar® /100% H_2SO_4 solutions examined via polarized light microscopy.

4. Two phase structure of 9.2% solution of Kevlar® /100% H_2SO_4 solution at 25°C examined via polarized light microscopy.

5. Anisotropic region of Kevlar® solutions.

   (a) Aggregated spherulitic structure at 9.5% and 25°C.
   (b) Nematic threadlike structures at 11% obtained on heating above 90 degrees C and cooling.

6. H_v laser small angle light scattering pattern for Kevlar® solution at 9.5%.

7. (a) Proposed arrangement of PPD-T macromolecules in the spherulites
   (b) Proposed arrangement of macromolecules in the nematic structure.

8. Viscosity as a function of shear rate in Kevlar®/H_2SO_4 solutions at 25 degrees C.

9. Normal stress versus shear rate relationship for Kevlar®/H_2SO_4 solutions at 25 degrees C.

10. Viscosity as a function of shear rate in Kevlar®/H_2SO_4 solutions at 60 degrees C.

11. Viscosity as a function of shear stress in Kevlar®/H_2SO_4 solutions at 25 degrees C.

12. Stable and unstable extrusion regions for Kevlar®/100% H_2SO_4 solutions.

13. Scanning electron microscope photomicrographs of ribbons.
    SEM photomicrographs of ribbons spun from 12% dope wet jet spinning with v_o = 0.014 m/min and v_1 = 0.37 m/min

    (a) Aspect ratio = 30; surface structure at 50x
    (b) Aspect ratio = 30; cross section at 500x
    (c) Aspect ratio = 16; cross section at 200x
    (d) Aspect ratio = 16; surface texture at 1800x.

14. WAXS patterns of the film

    (a) with uniaxial extension
    (b) with biaxial extension

15. Engineering stress-strain curves for machine and transverse directions of films extruded through an air gap using an 12% PPD-T Kevlar® /H_2SO_4 solution.

    (a) Blow up ratio = 1.2x
    (b) Blow up ratio = 1.0x

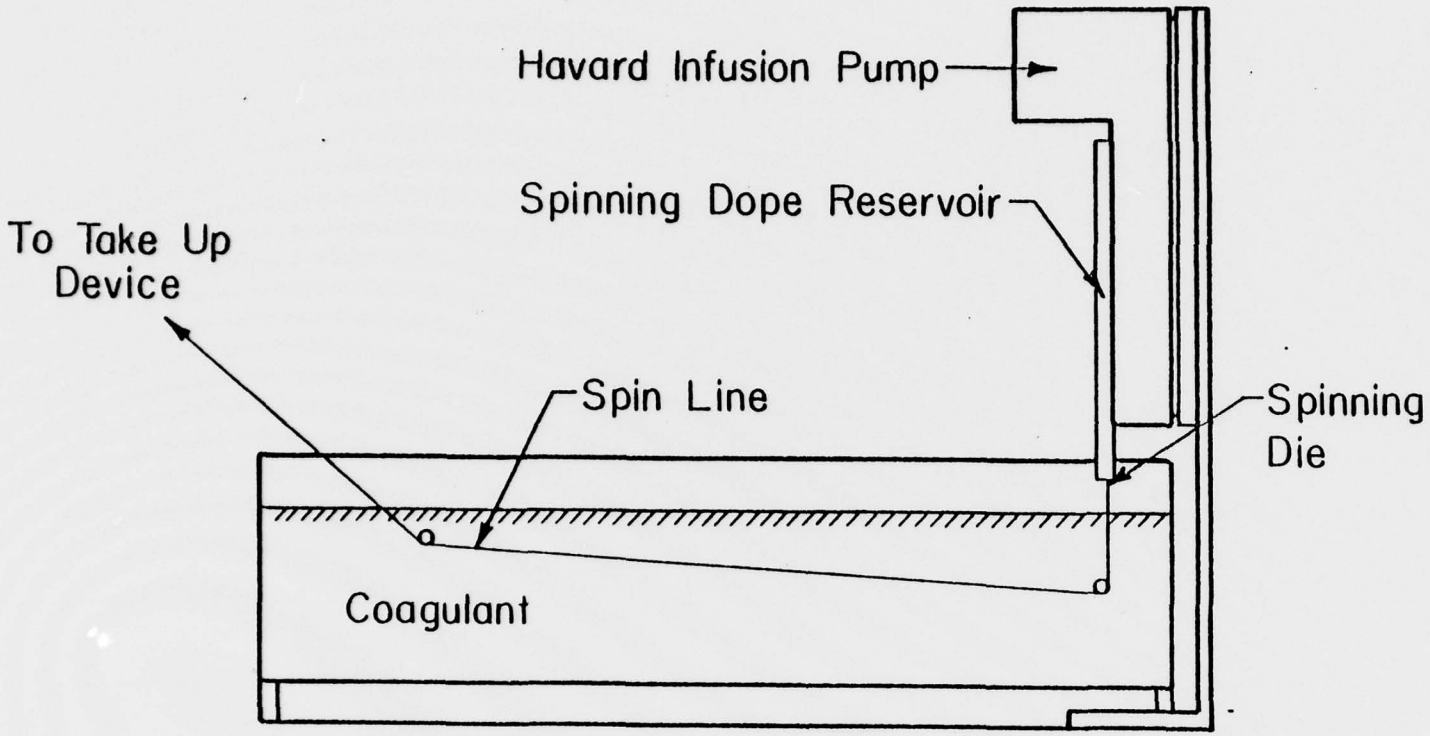


FIGURE 1. (A) SMALL SCALE EXTRUSION APPARATUS.
USED IN THE APPARATUS.

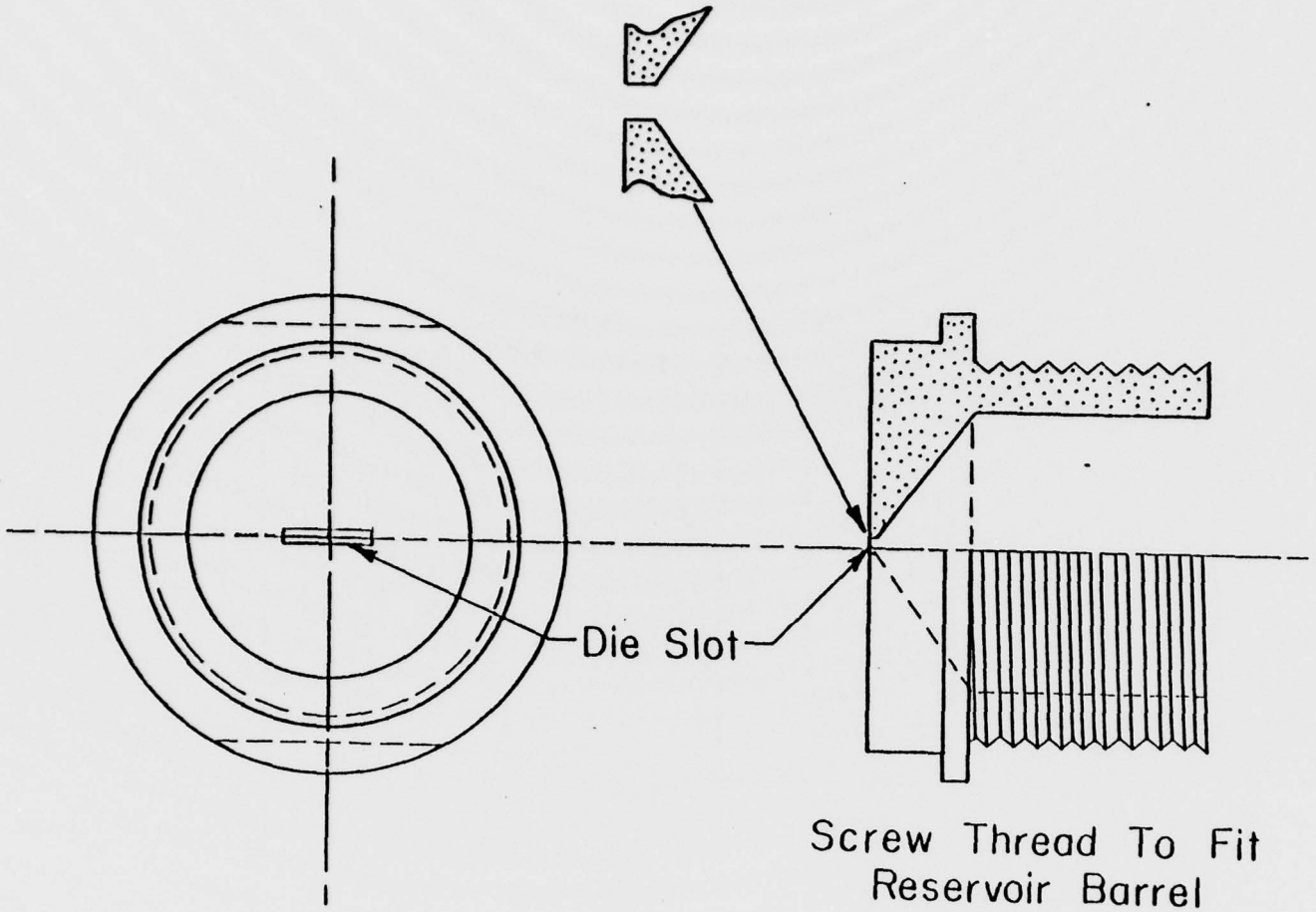


FIGURE 1. (B) RIBBON SLIT DIE

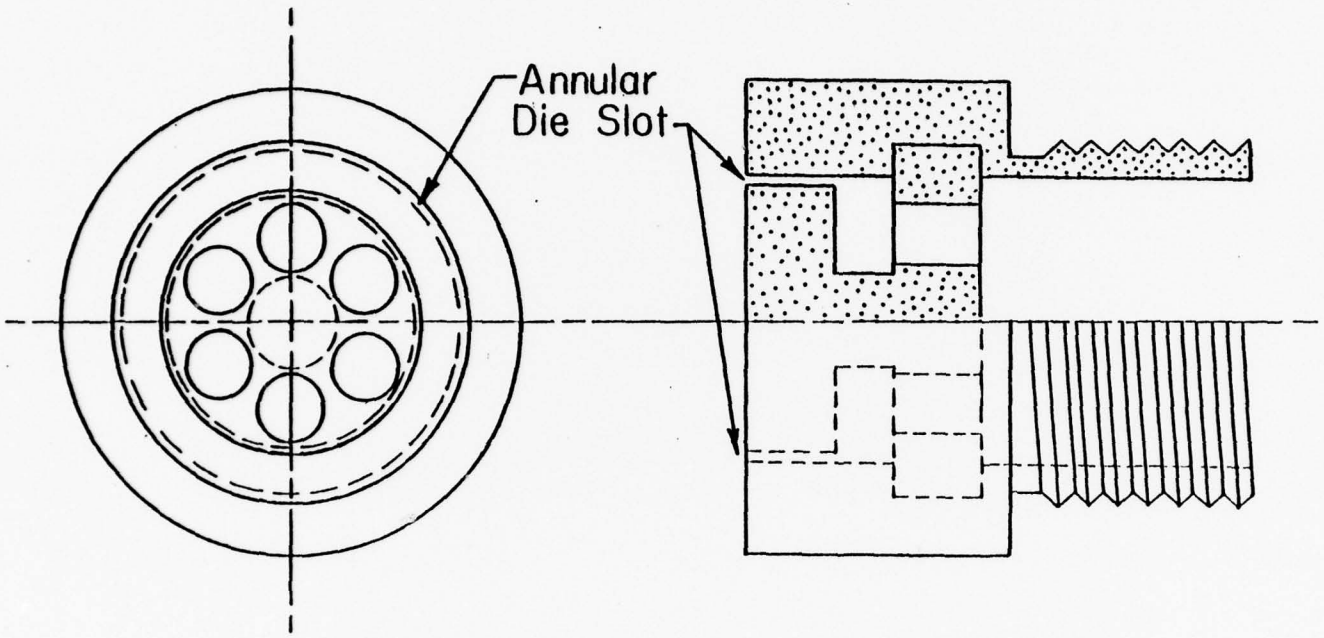


FIGURE 1. (c) ANNULAR DIE USED IN THE APPARATUS.

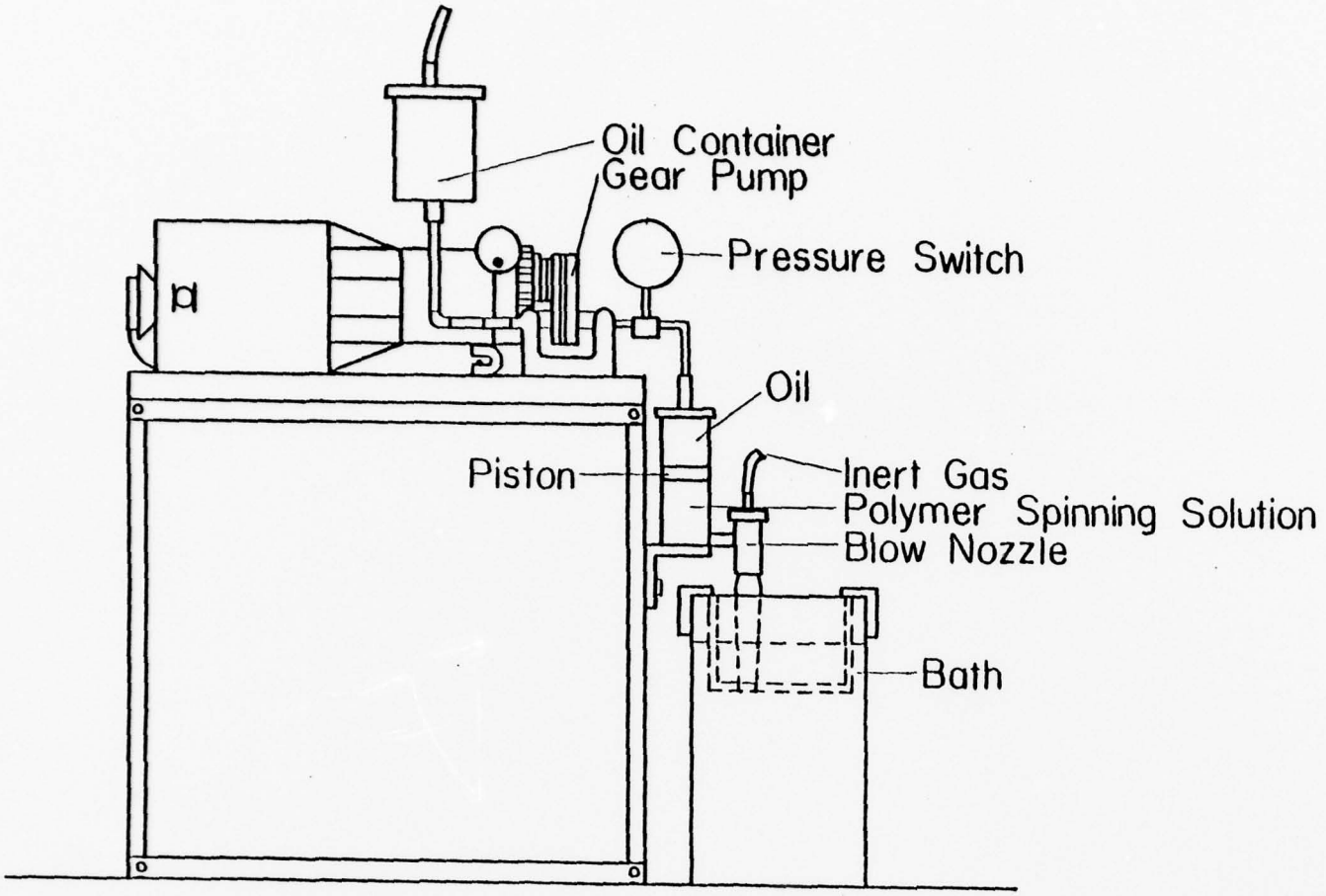


FIGURE 2. (A) TUBULAR FILM EXTRUSION APPARATUS.

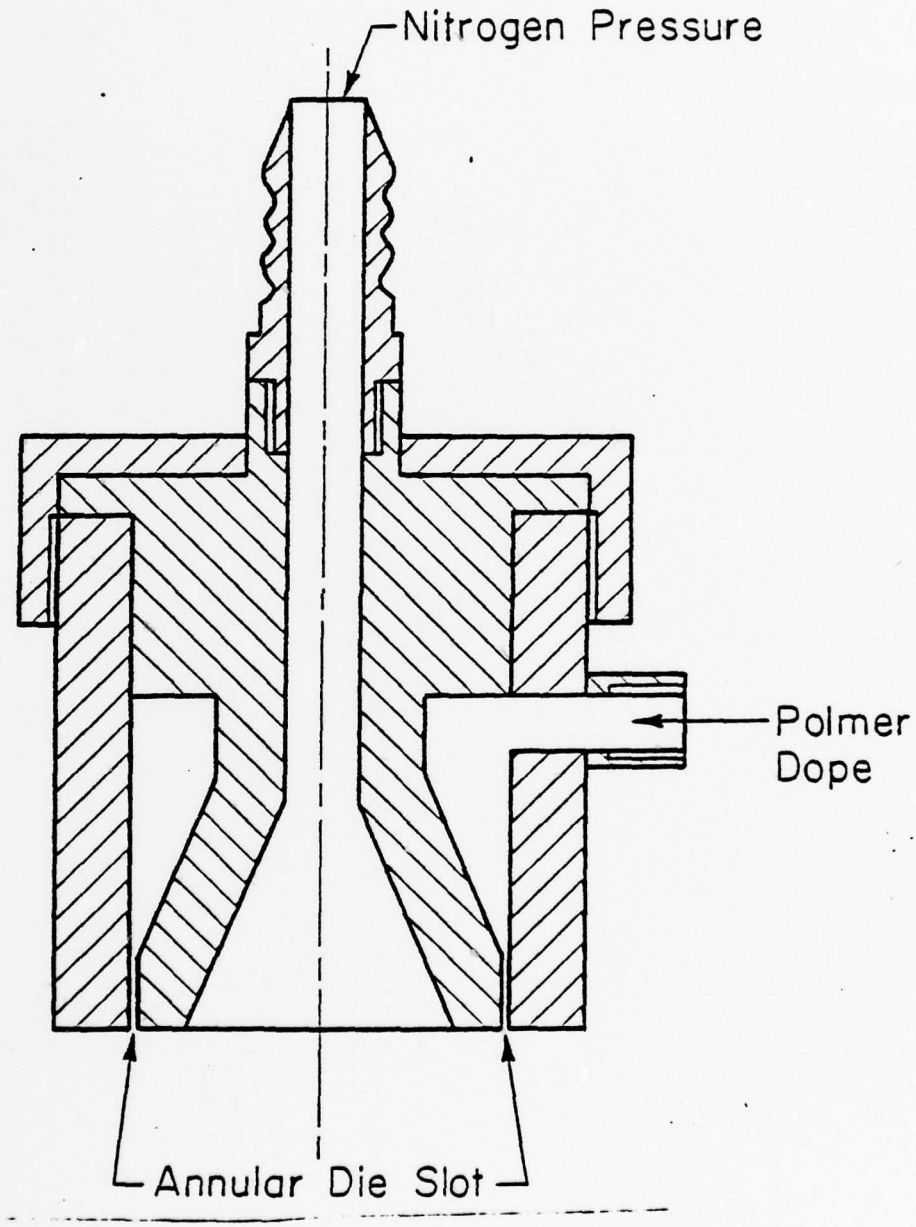


FIGURE 2. (B) TUBULAR FILM DIE.

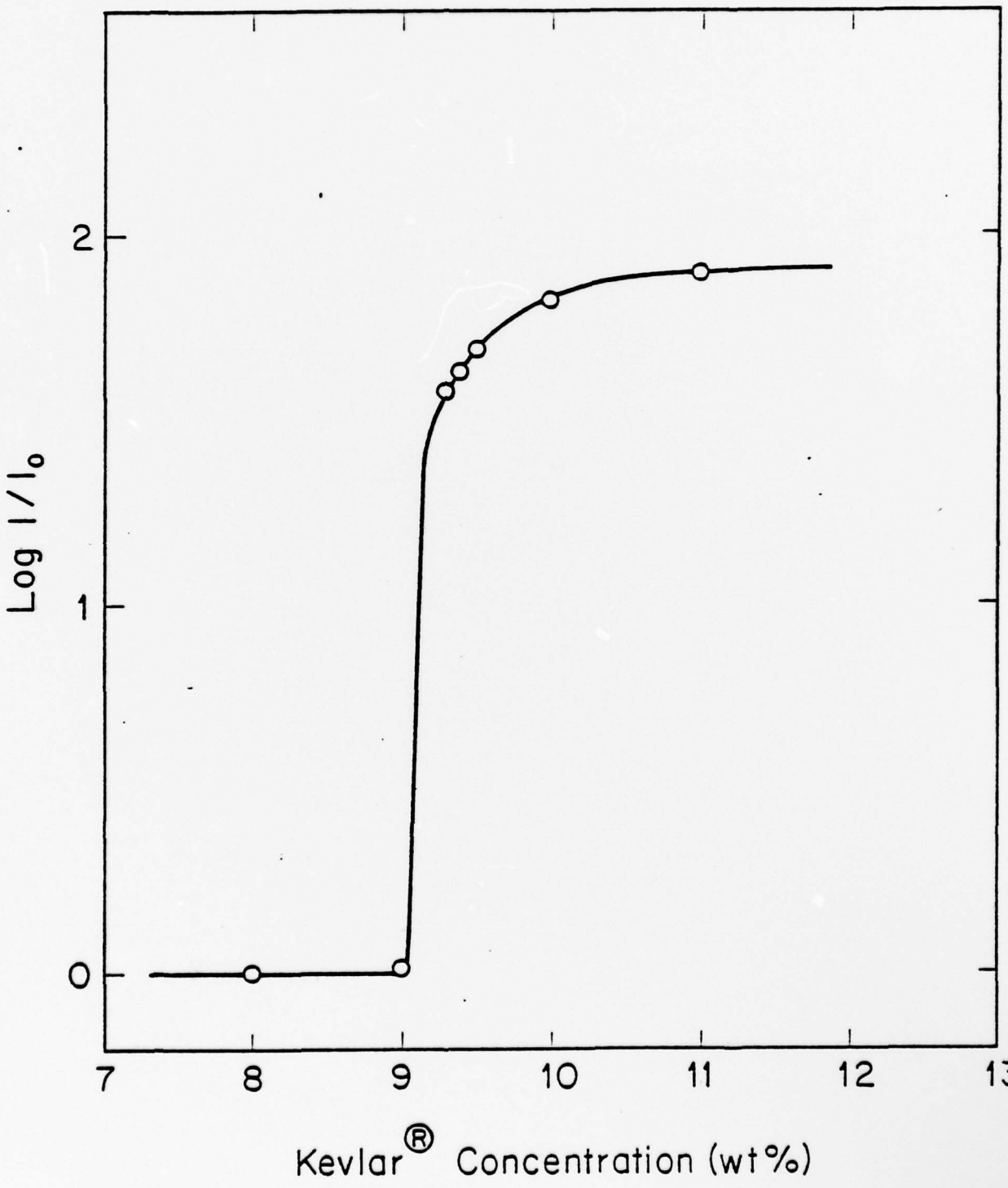
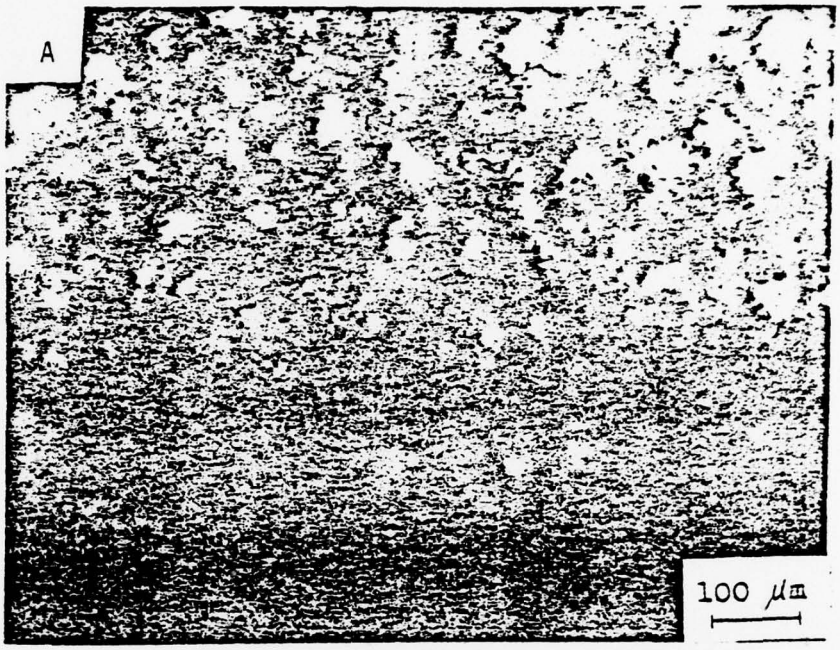
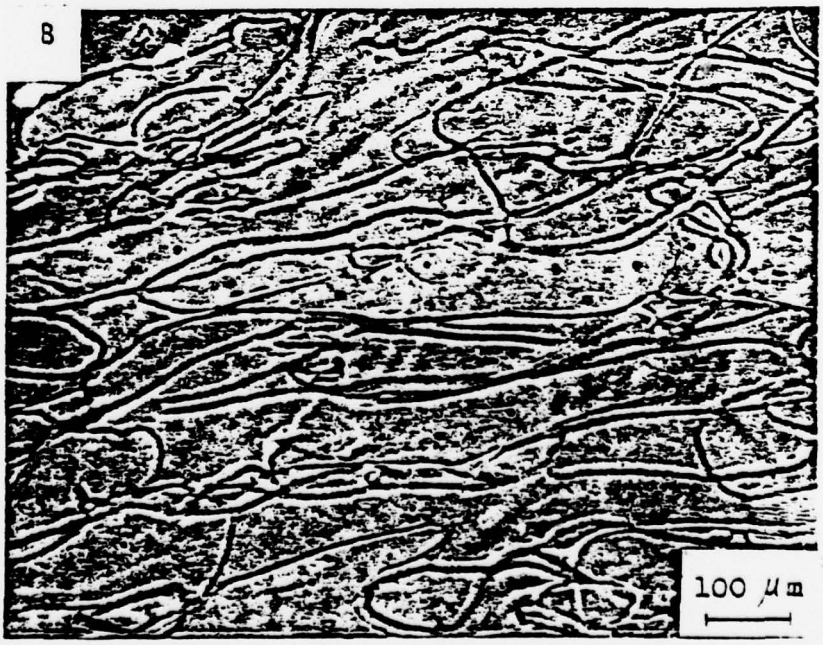


FIGURE 3. LIGHT INTENSITY AS A FUNCTION OF CONCENTRATION FOR KEVLAR® / 100% H_2SO_4 SOLUTIONS EXAMINED VIA POLARIZED LIGHT MICROSCOPY.

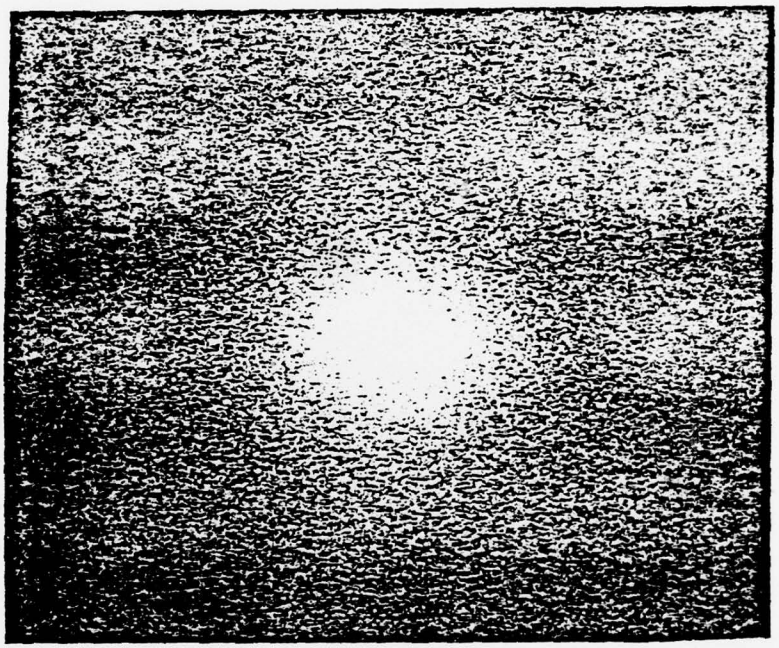
4. Two phase structure of 9.2% solution of Kevlar® /100% H_2SO_4 solution at 25°C examined via polarized light microscopy.



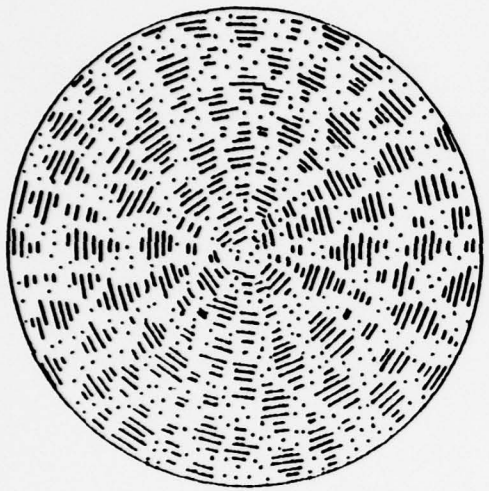


5. Anisotropic region of Kevlar® solutions.

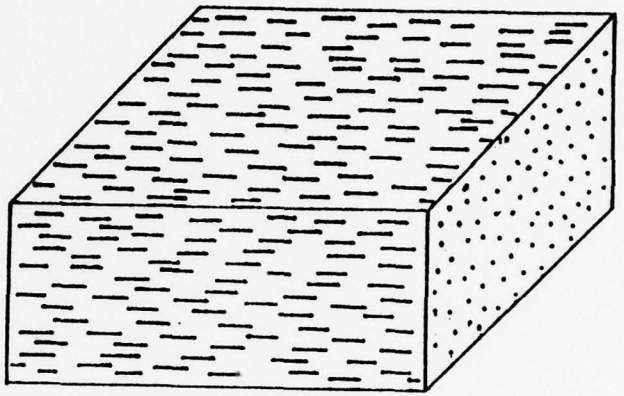
(a) Aggregated spherulitic structure at 9.5% and 25°C.
(b) Nematic threadlike structures at 11% obtained on heating above 90 degrees C and cooling.



6. H_v laser small angle light scattering pattern for Kevlar® solution at 9.5%.

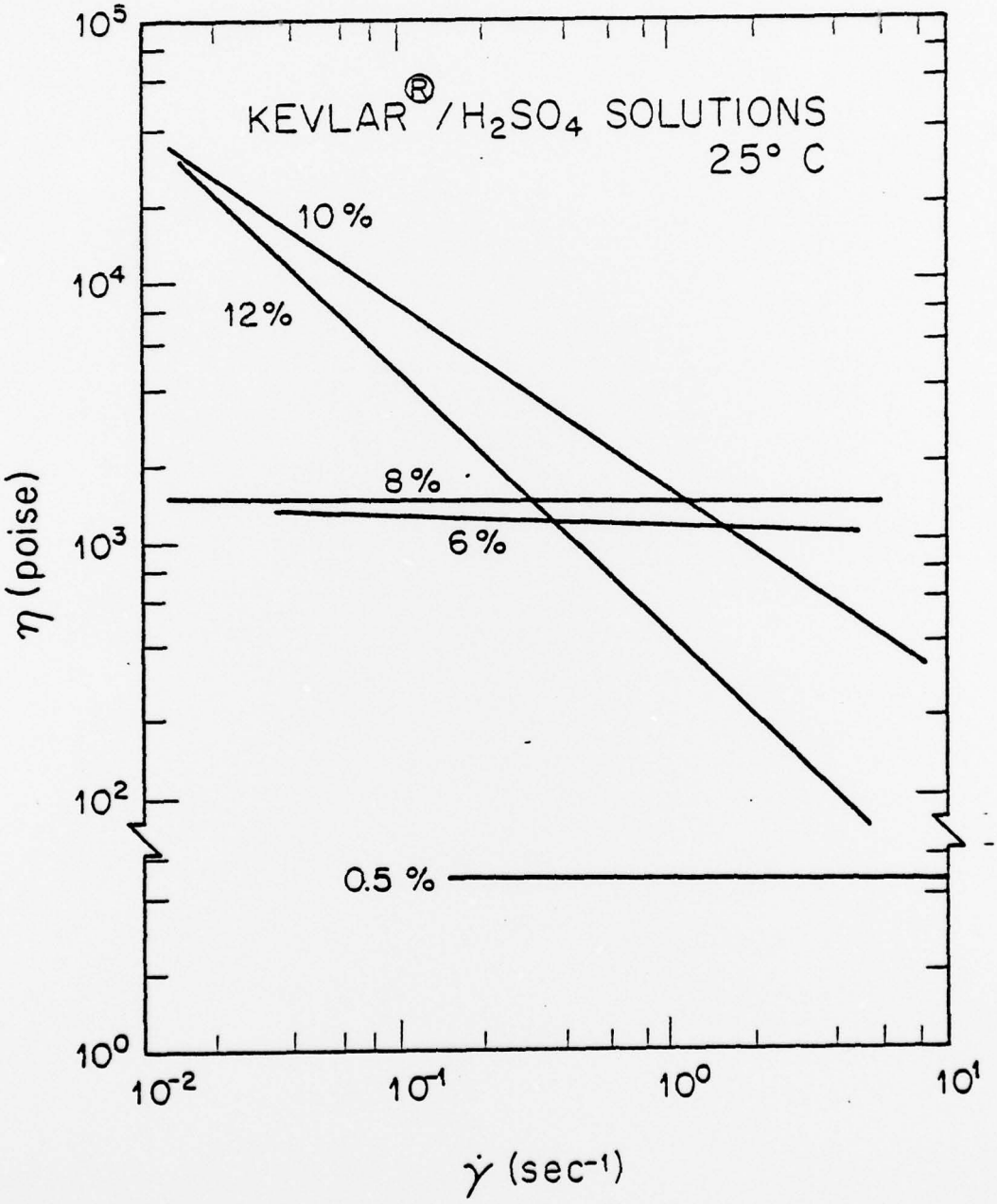


a

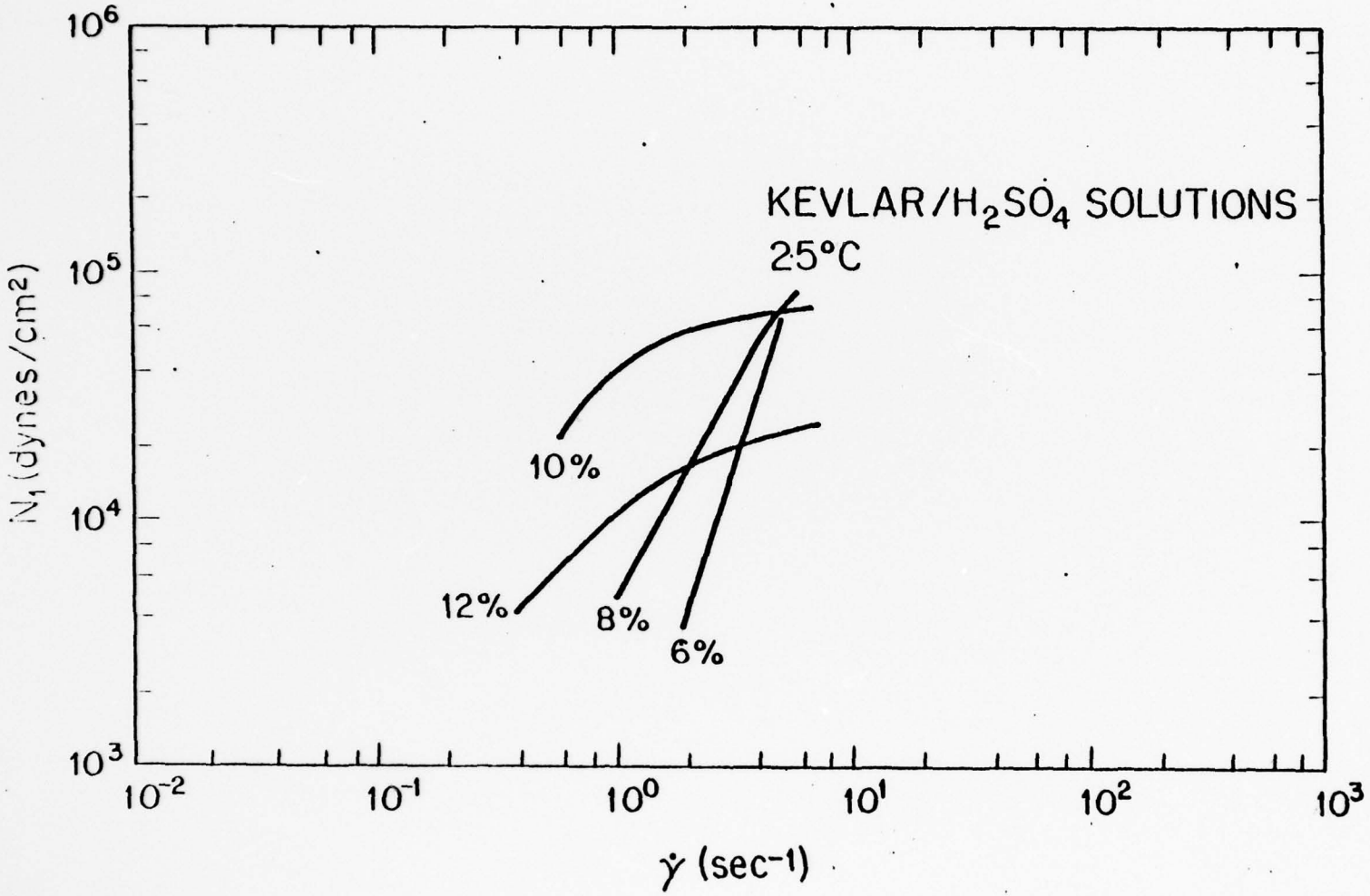


b

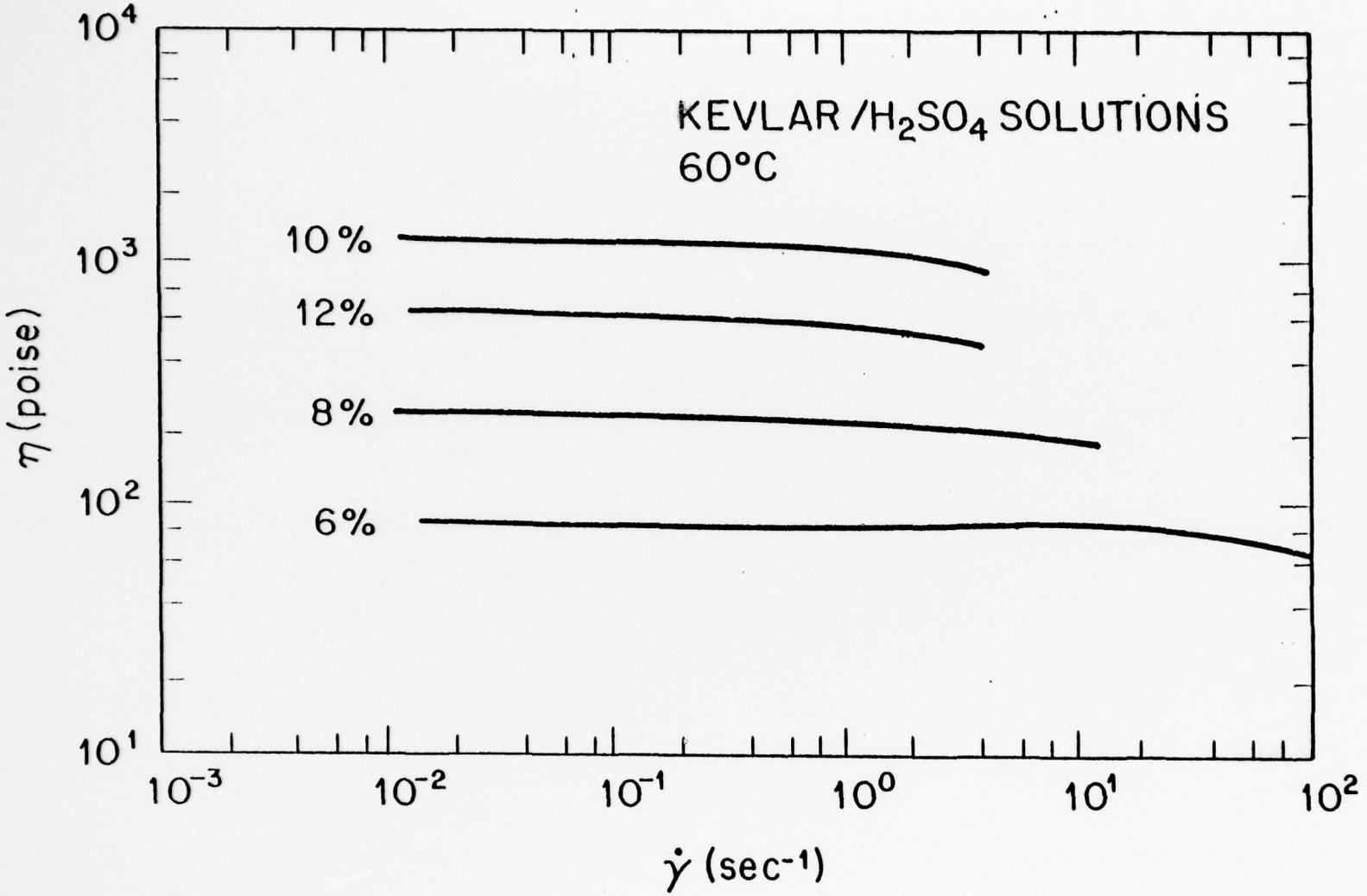
7. (a) Proposed arrangement of PPD-T macromolecules in the spherulites
   (b) Proposed arrangement of macromolecules in the nematic structure.



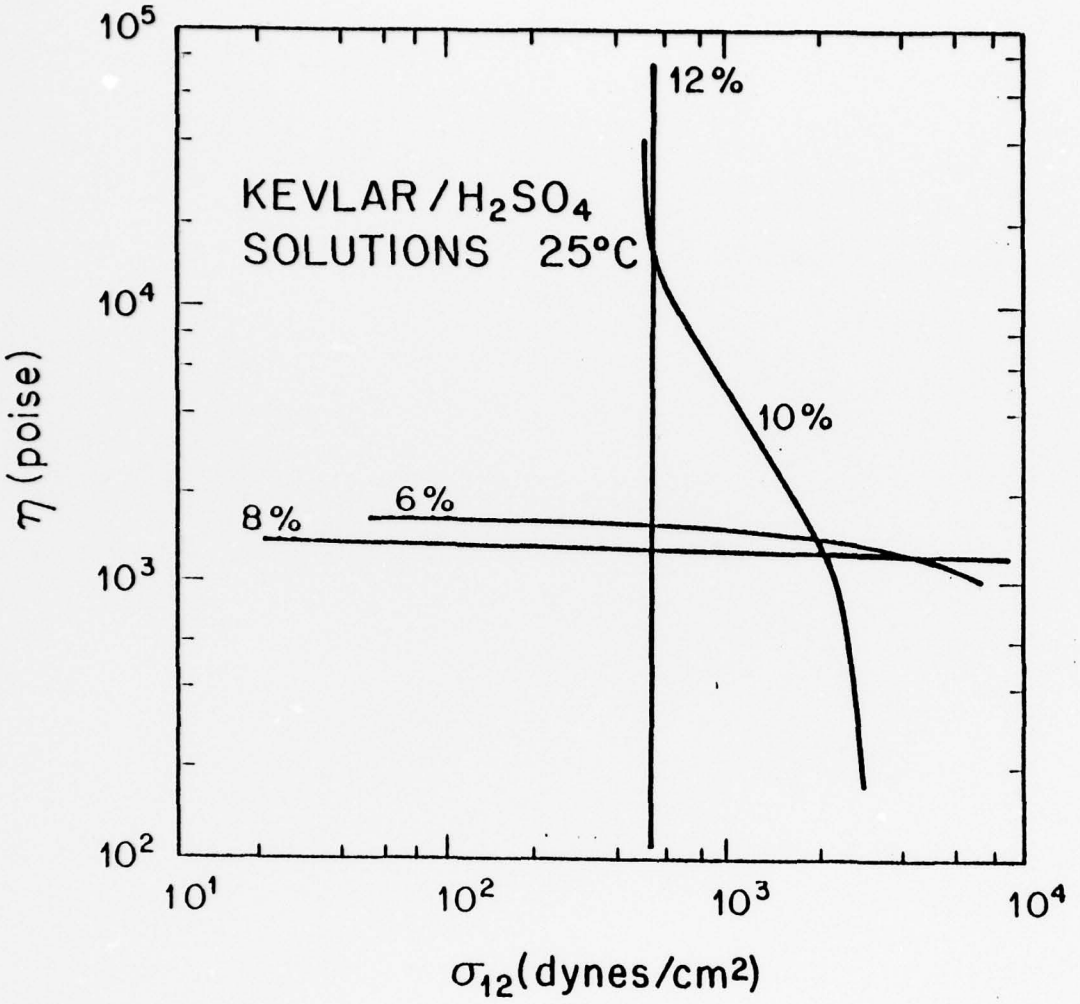
8. Viscosity as a function of shear rate in Kevlar®/H_2SO_4 solutions at 25 degrees C.



9. Normal stress versus shear rate relationship for Kevlar®/H_2SO_4 solutions at 25 degrees C.



10. Viscosity as a function of shear rate in Kevlar® /H_2SO_4 solutions at 60 degrees C.



11. Viscosity as a function of shear stress in Kevlar® /H_2SO_4 solutions at 25 degrees C.

THE AREAS BENEATH AND TO THE RIGHT OF THE LINES ////////// INDICATE WHERE EXTRUDATE DISTORTION OCCURS.

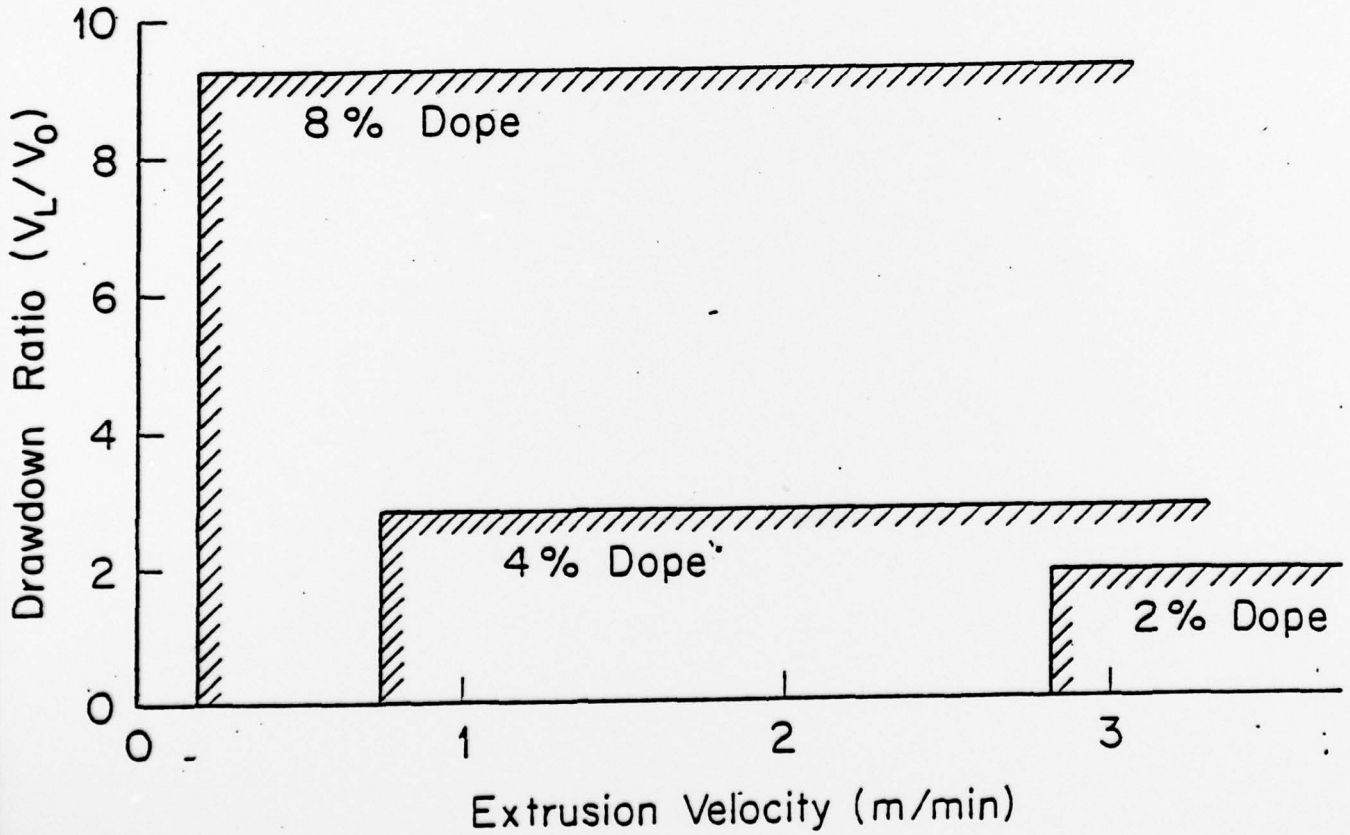
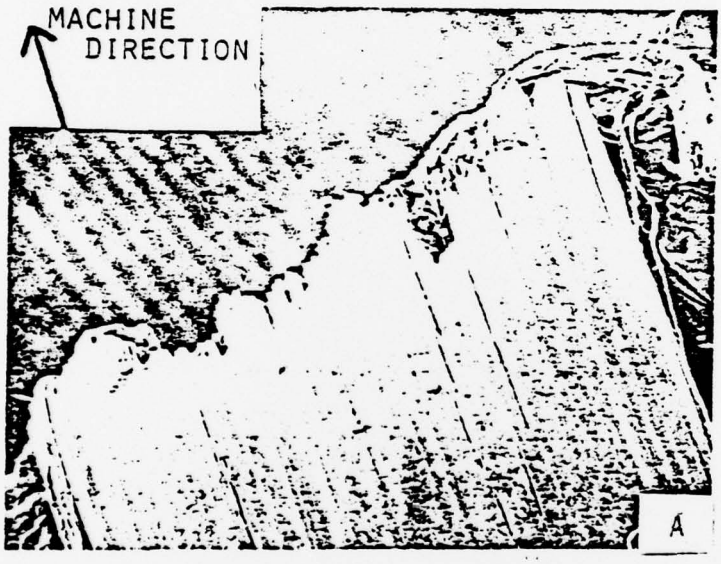


FIGURE 12. STABLE AND UNSTABLE EXTRUSION REGIONS FOR KEVLAR ® / H_2SO_4 SOLUTIONS.

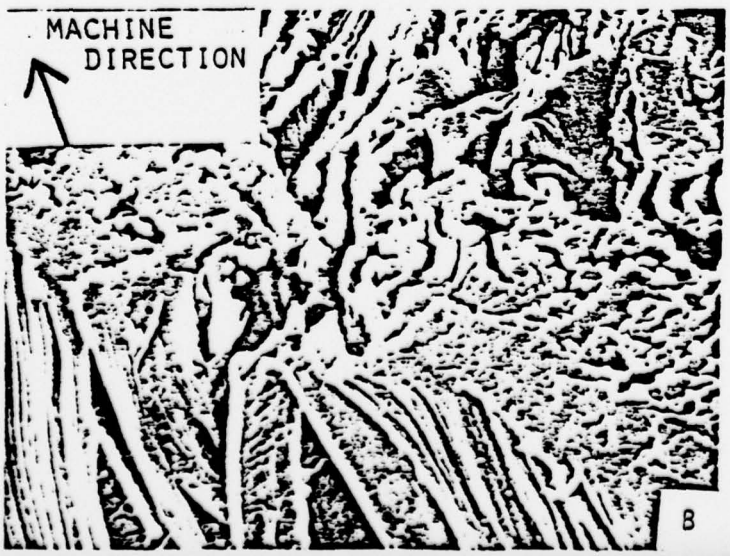
FIGURE 13

SEM PHOTOMICROGRAPHS OF RIBBONS SPUN FROM 12% DOPE WET JET SPINNING WITH V_0=0.014M/MIN AND V_1=0.37 M/MIN

ASPECT RATIO = 30
SURFACE STRUCTURE AT 50X



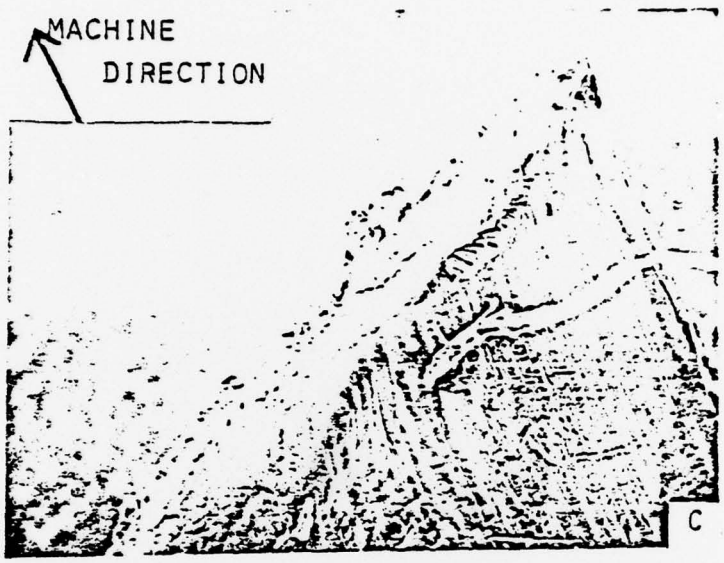
ASPECT RATION = 30
CROSS SECTION AT 500X



(FIGURE 13)

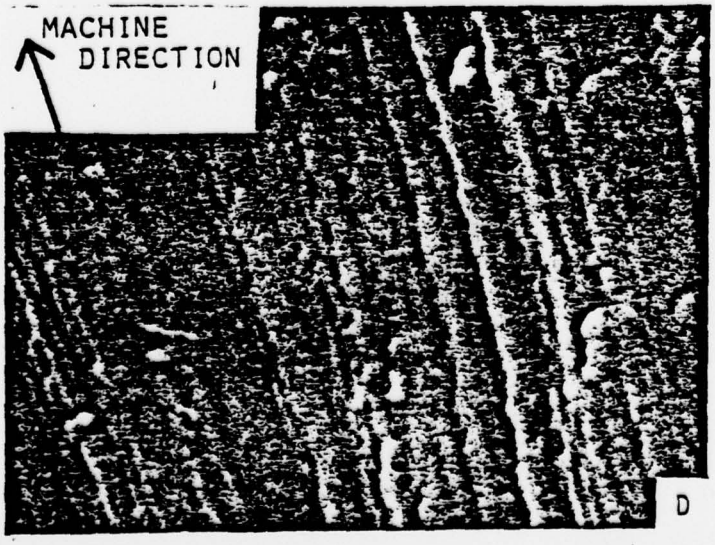
ASPECT RATIO = 16

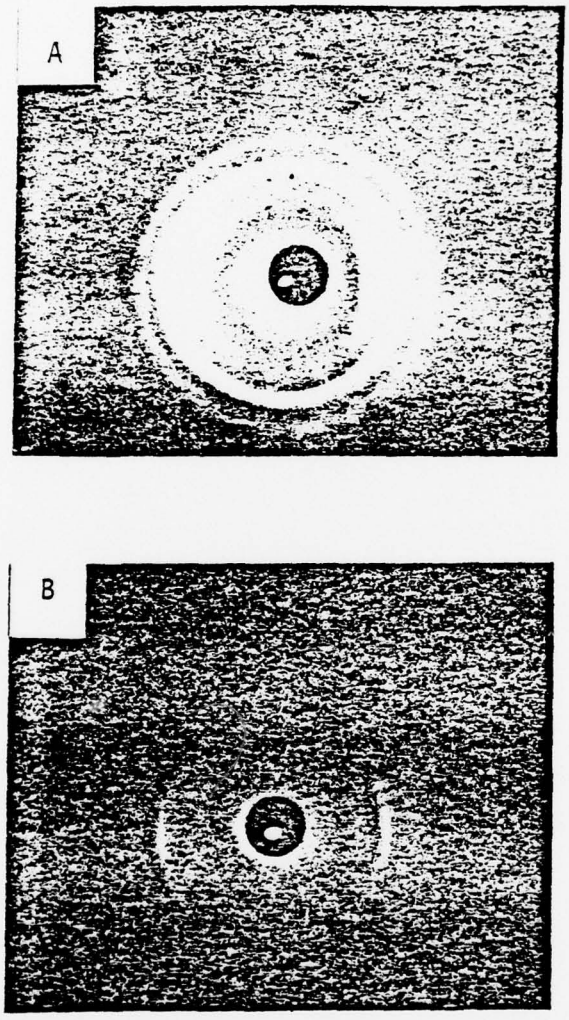
CROSS SECTION AT 200X



ASPECT RATIO = 16

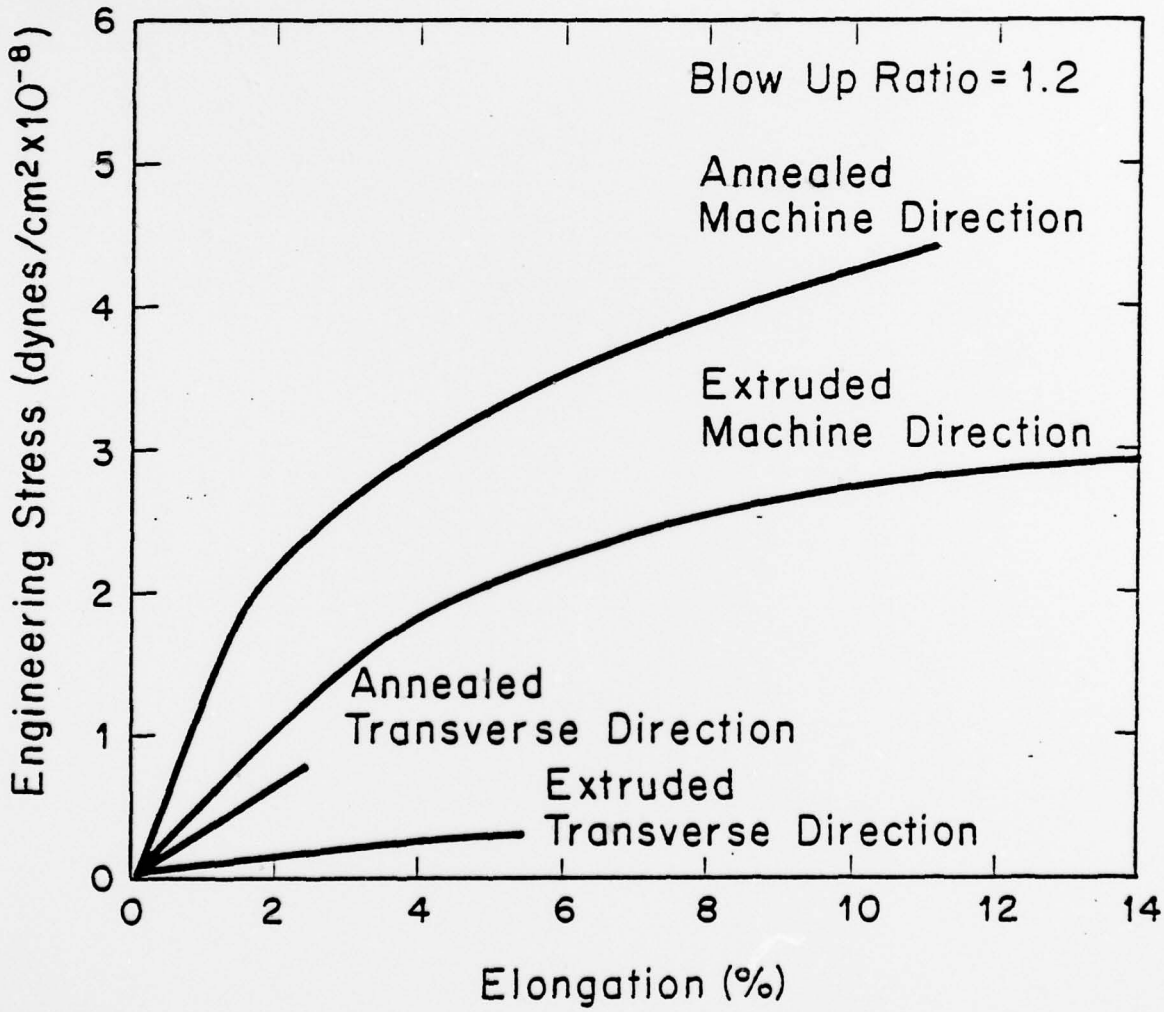
SURFACE TEXTURE AT 1800X





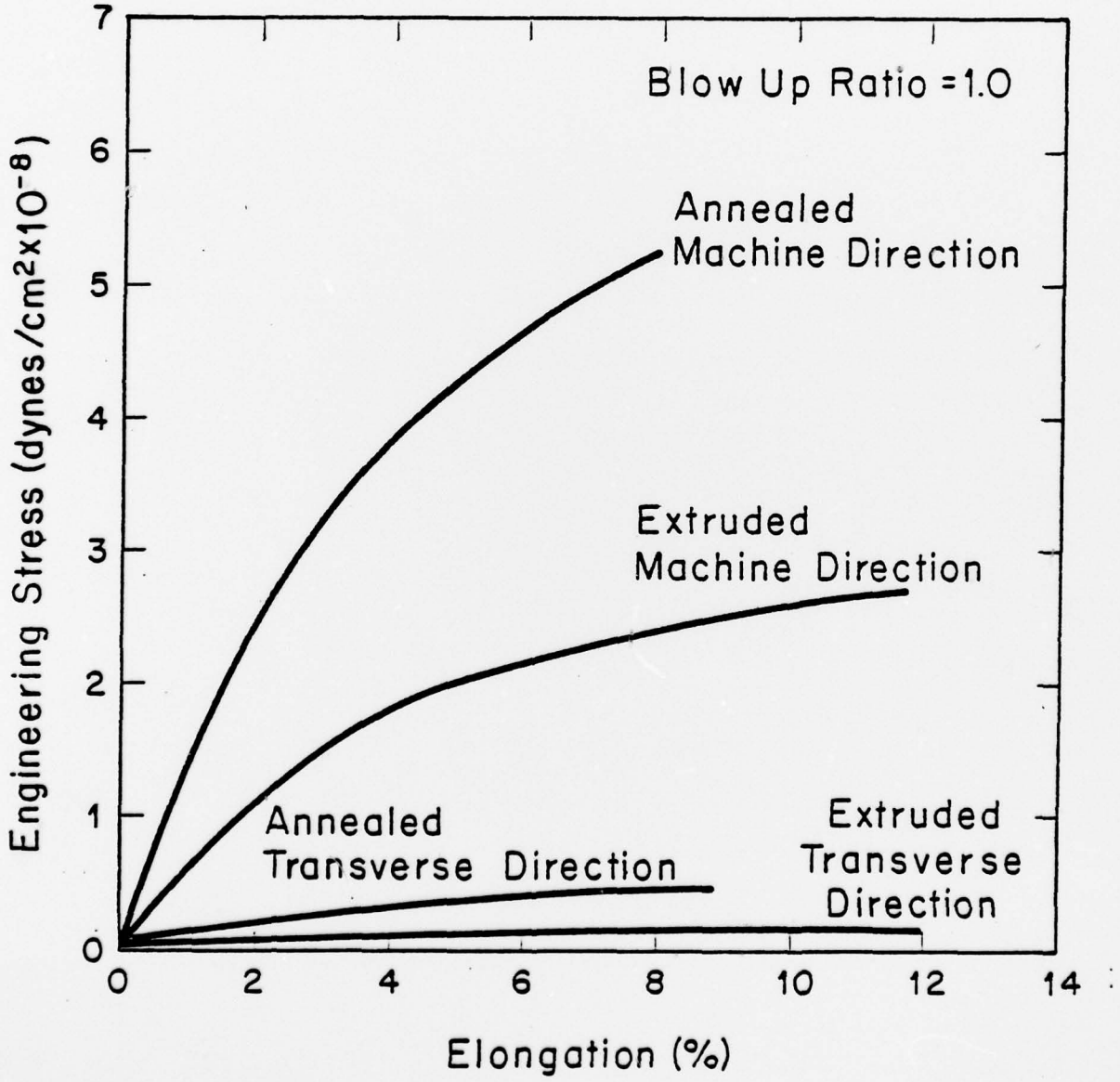
14. WAXS patterns of the film

(a) with uniaxial extension
(b) with biaxial extension



15. Engineering stress-strain curves for machine and transverse directions of films extruded through an air gap using an 12% PPD-T Kevlar® /H_2SO_4 solution.

(a) Blow up ratio = 1.2x



15. Engineering stress-strain curves for machine and transverse directions of films extruded through an air gap using a 12% Kevlar ®/H_2SO_4 solution.

(b) Blow up ratio = 1.0x